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(54) **Mass spectra analysis of gases**

(57) **Mass spectra analysis of gases supplied simultaneously or sequentially in a carrier gas to the spectrometer where a first component of the gases has a different volume ratio with respect to the carrier compared to a second component is characterised by decreasing the concentration of the component with the larger volume ratio by an additional supply of carrier gas thereto. Apparatus operating on the "open split" system and characterised by provision of an additional diluting line for the carrier gas is also disclosed.**

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FIG. 1

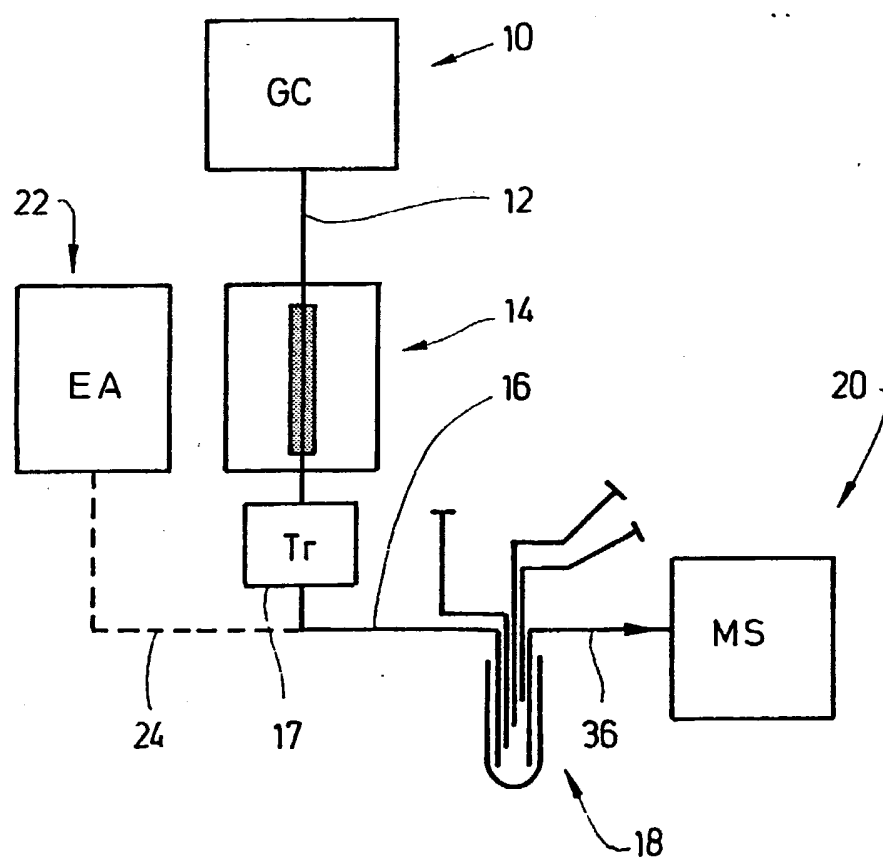
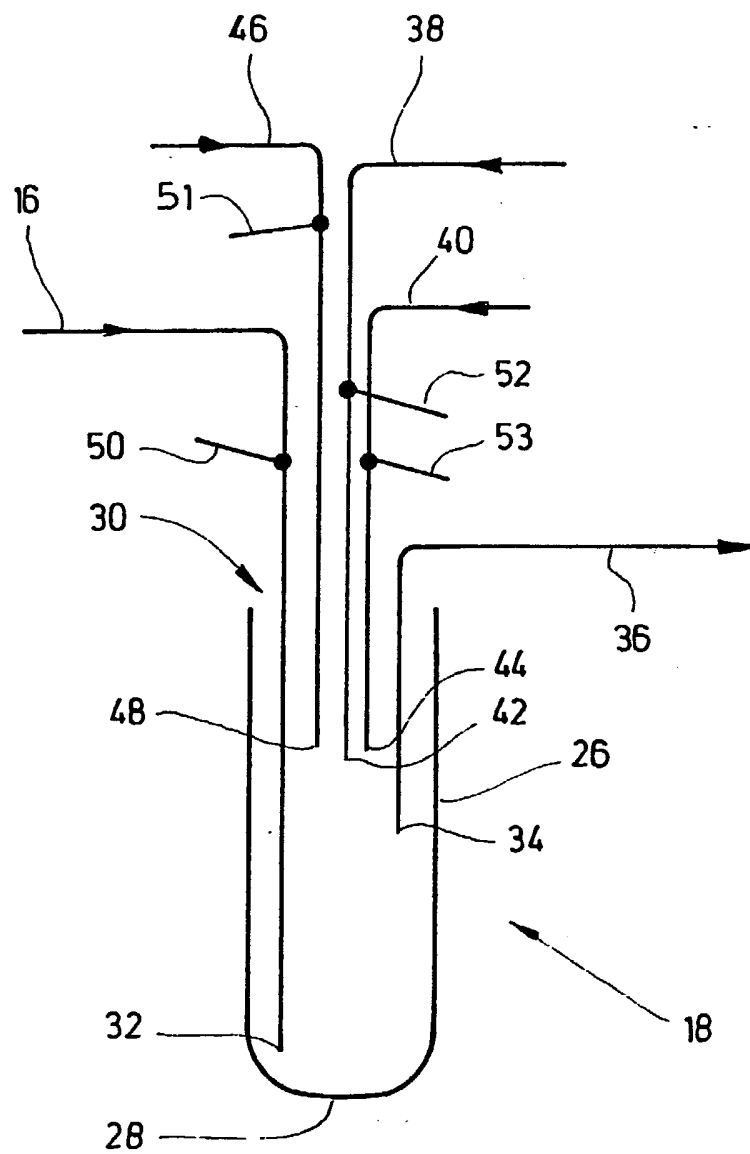


FIG. 2



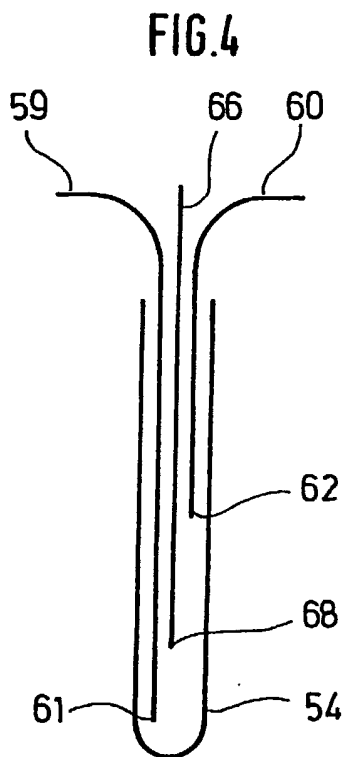
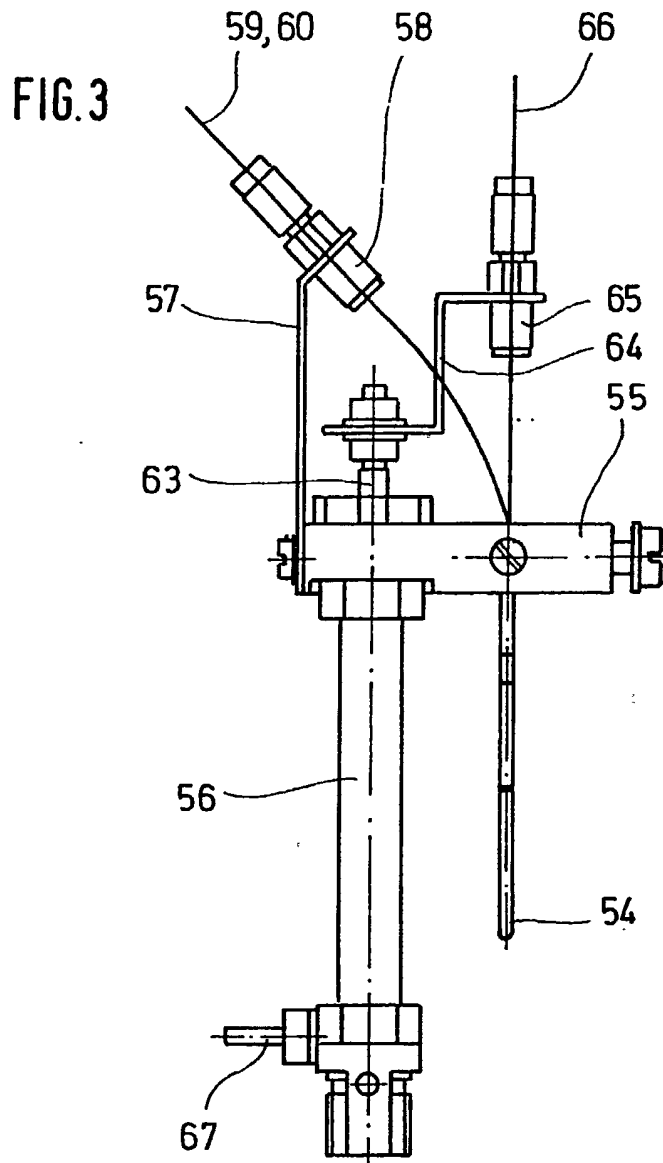


FIG.5

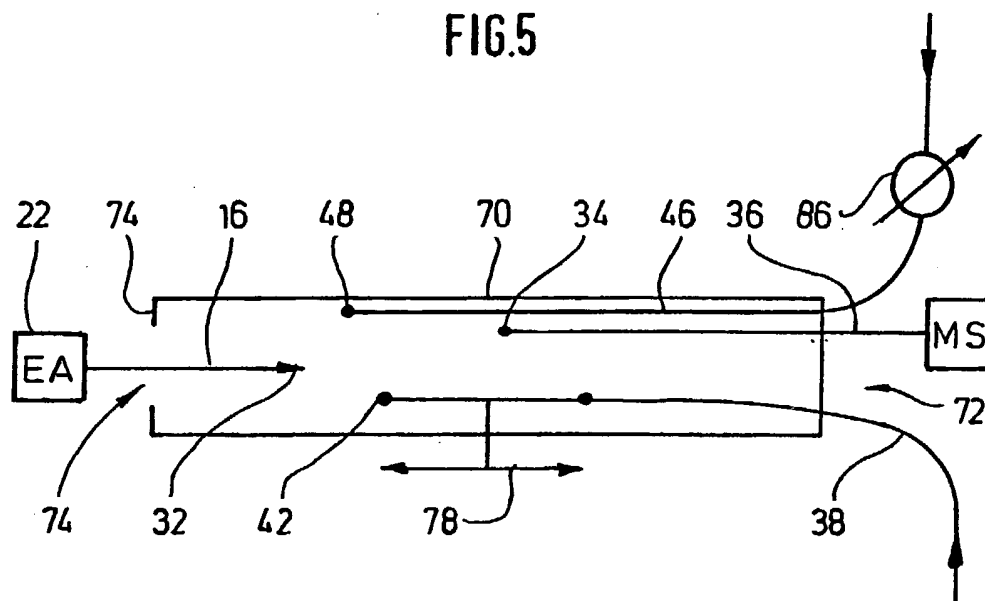
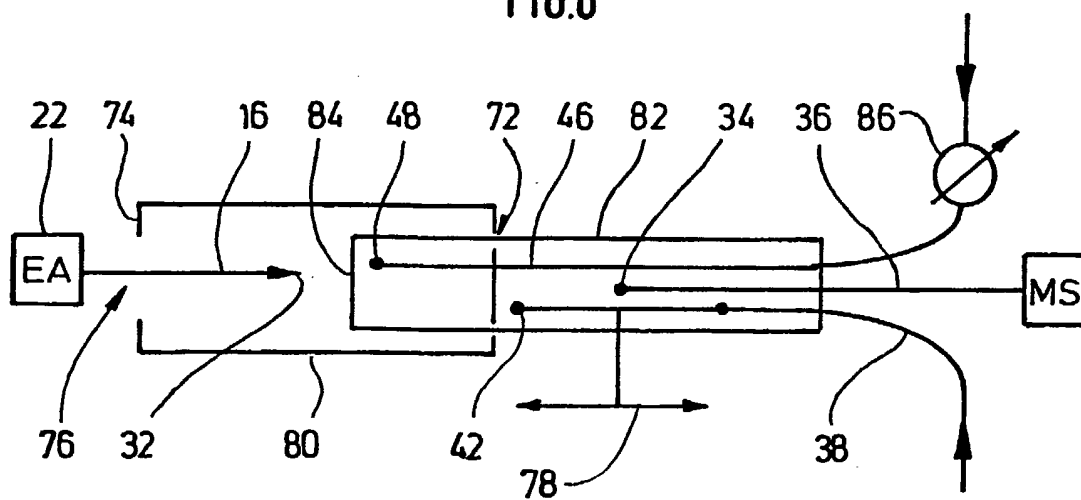


FIG.6



Process for the analysis of gaseous components by mass
spectrometry

D e s c r i p t i o n :

- 1 The invention relates to a process for the analysis of
several, especially two, gaseous components by mass
spectrometry, the components being supplied, simultaneously
or successively, with a carrier gas to a mass spectrometer,
5 the first component having a different volume ratio
relative to the carrier gas compared to the second
component. Furthermore, the invention relates to an
apparatus for the provision of gaseous samples for an
analysis by mass spectrometry, especially for conducting
10 the process.

Background of the invention and its preferred field of
application is the isotope-ratio analysis by mass
spectrometry, especially of carbon and nitrogen or, for
example, of sulphur. In the course of a so-called
GC-IRMS-analysis, for example, organic compounds or

1 compound mixtures can be separated in a gas chromatograph
(GC) and the separated components can be decomposed in a
downstream combustion oven. If the organic compound or the
compound mixture contains carbon, hydrogen and nitrogen,
5 CO_2 , H_2O and N_2 are formed in the combustion oven by
oxidation. In this case, it is relevant to determine the
isotope ratios $\text{C}12/\text{C}13$ of the CO_2 and $\text{N}14/\text{N}15$ of the N_2 .
This is attained by means of the downstream mass
spectrometer, the sample gases CO_2 and N_2 being allowed to
10 flow in on-line into the ion source of the mass
spectrometer. The principle of the method is described, for
example, in Analytical Chemistry, Vol. 50, Nr. 11,
September 1978, pages 1465-1473 and in Org. Chem., Vol 16,
Nr. 5-6, pages 1115-1128. Sometimes this analytical method
15 is also abbreviated IRM-GCMS. Utmost precision is required
in such analyses. In order to attain the required
precision, the sample gases (CO_2 and N_2) are allowed to
reciprocally flow into the mass spectrometer with a
standard gas of which the isotope ratio is known. In the
20 measurements, only the deviation of the isotope ratio of
the sample relative to the standards is important. The
deviations may be extremely small.

During a measurement, alternately CO_2 or N_2 and
25 corresponding reference gases, i.e. CO_2 and N_2 having a
standard isotope ratio, are supplied to the mass
spectrometer. Normally, the quantity of CO_2 produced in the
analysis of organic compounds is much higher than the
quantity of N_2 (20:1 to 50:1). If the gases were allowed to
30 flow into the MS in this ratio of concentration, ion
currents of very different sizes would be generated for CO_2
and N_2 . A mass spectrometer, however, operates at its
optimum only in a certain range of ion current. It is,
therefore, expedient to adjust the ion currents to one
35 another. This can not be achieved by simply reducing the
gas inflow of CO_2 , for example by means of a throttle
valve. A change in the throttling of the gas inflow always
causes a change (even if only a small one) of the isotope

1 ratio (fractionation). A further problem arises: carrier
gas (preferably helium) flows into the mass spectrometer
together with the sample gas. The concentration of the
carrier gas is substantially higher than that of the sample
5 gas. This carrier gas is ionized in the ion source of the
mass spectrometer together with the sample gas and produces
a relatively high volume charge. As a change in the
throttling of the gas inflow equally affects sample gas and
carrier gas, the volume charge would be changed thereby.
10 The volume charge, however, influences the ion-optical
properties of the mass spectrometer (focusing of the ions)
and, therefore, has to be held constant in precision
measurements of isotope ratios. This is another reason why
a change of the gas inflow would be very inappropriate.

15 The object of the present invention is to create a process
or an apparatus which allows an isotope-ratio analysis which
is as precise as possible.

20 The process according to the invention is characterized in
that, in the analysis of a component which has the greater
concentration with respect to the carrier gas, the
concentration of this component is reduced by supplying
additional carrier gas. Accordingly, in the analysis of CO_2
25 in connection with helium as a carrier gas, the sample gas
is diluted with additional helium. Thereby, the
concentrations of the sample gases in the carrier gas can
be approximated to one another, so that the negative
effects different concentrations of the sample gases have
30 on the precision of measurement can be avoided. The total
gas inflow is practically not affected by the addition of
helium, because it is determined exclusively by the
throttling effect of the inflow capillaries in the mass
spectrometer. If the sample or component to be analyzed
35 contains CO_2 and N_2 , successive measurements are conducted
in the mass spectrometer, for example a determination of
the isotope ratio of the N_2 first, and a subsequent
measurement of the CO_2 . Each measurement is compared to the

1 standard samples.

Known per se is the principle of an open split before the entry of the gases to be analyzed in the ion source of the mass spectrometer. A fraction of the gases emerging from a line is transferred almost under atmospheric pressure to a further line. The largest portion of the gases to be analyzed is discharged as excess and thereby displaces possible secondary air flows. Advantageously, the dilution with additional carrier gas takes place in the region of this open split. The additional carrier gas does not influence the pressure ratio and flow conditions. Merely the ratio of carrier gas and gas to be analyzed is changed, especially of helium and CO₂.

15 The dilution appropriately takes place in such a manner that the concentrations of the gases to be analyzed (CO₂ or N₂) become approximately equal. To be more specific, after dilution the quantity of CO₂ in the CO₂-analysis corresponds to the quantity of N₂ in the N₂-analysis. For this reason the isotope-ratio analysis can be carried out with very high precision.

25 Starting out from an apparatus according to the preamble of the independent apparatus claim, the apparatus according to the invention is characterized in that a further supply line (dilution line) is provided, via which a further gas, in addition to the other gases emerging from the other supply lines, can be supplied to the throttle line. This apparatus makes it possible to carry out the above-mentioned process.

35 Further features of the invention are to be found in the subclaims and the description. Exemplary embodiments of the invention are explained in detail hereinafter by means of the drawings. In these:

1 Fig. 1 shows a diagrammatic representation of a system
for conducting an isotope-ratio analysis,

5 Fig. 2 shows an enlarged detail of Fig. 1, namely a
so-called open split in an embodiment according
to the invention,

10 Fig. 3 shows an open split for the demonstration of the
movement of the capillaries,

10 Fig. 4 shows the basic structure of the open split
according to Fig. 3,

15 Fig. 5 shows a further embodiment of an open split in a
representation similar to Fig. 2,

Fig. 6 shows a variation in a representation similar to
Fig. 5.

20 The system shown in Fig. 1 is provided for conducting an
isotope-ratio analyses by mass spectrometry. Two different
embodiments are explained by means of the same figure. The
point of departure is a gas chromatograph 10 (GC). A
component of the sample contained therein and separated
25 from the other components, for example an amino acid, is
supplied to a combustion oven 14 via a line 12 and is
oxidated therein. The combustion products resulting
therefrom are separated in time via a gas supply line 16 in
a second gas chromatograph 17 designated "Tr" for the
30 separator in Fig. 1. Finally, the combustion products are
supplied to a so-called open coupling (open split) 18 of
the ion source of a mass spectrometer 20 (MS) comprising a
multiple collector. For the analysis of CO₂, for example a
double collector can be employed, that is to say one
35 collector each for the ions with the mass number 44 (C12)
and 45 (C13), respectively. This type of analysis - without
the second gas chromatograph 17 - is known as IRM-GCMS
(Isotope-Ratio-Monitoring Gas-chromatography-Mass

1 Spectrometry) or as GC-IRMS (Gas-chromatography Isotope
Ratio Mass Spectrometry). Corresponding to the schematic
representation in Fig. 1, further details necessary for the
analysis, for example valves or additional supply lines,
5 are not shown if they are not directly related to the
invention.

In another, very important application, a so-called element
analyzer (EA) 22 or CHN-analyzer is employed instead of
10 structural components 10, 12, 14, 17. A combustion oven and
a GC are integrated in the EA. For example solid samples
are fed into the EA and burned therein. Gases which are
formed during combustion are separated in time, emerge one
after another and thus can be fed one after another, via a
15 supply line 24, to the line 16 which is connected to the
open split 18.

The open split 18 is shown in more detail in Fig. 2 and
takes the form of a small coupling tube 26 open at one side
20 with a closed bottom 28 and an open end face 30. The gas
emerging from the gas chromatograph or the combustion oven
is piped into the region of the bottom 28 via a supply line
16 with a corresponding opening 32. The gas is discharged
via an opening 34 of a snifting or throttling line 36 which
25 leads to the mass spectrometer, said opening 34 being
located approximately centrally relative to the height of
the small tube 26 (above the opening 32). The object is to
determine the isotope ratios for carbon and nitrogen in the
gases CO_2 and N_2 contained in one or various samples.
30 Accordingly, two supply lines 38, 40 are provided for
reference samples with exactly defined isotope ratios of
the mentioned gases. Openings 42, 44 of the supply lines
38, 40 also end inside of the small coupling tube 26.

35 In connection with the invention particular emphasis is
given to a further supply line, namely a dilution line,
which has an opening 48 that ends in the small coupling
tube 26. Additional carrier gas can be supplied by this

1 small coupling tube 26.

For controlling the gas inlet into the opening 34 by
varying immersion of the lines 46, 38 and/or 40, said lines
5 are axially moveable. A mechanical device provided for this
purpose is outlined by appropriate levers 51, 51, 53 in
Fig. 2. These can be operated separately or in groups, so
that the corresponding openings 48, 42, 44 are variable in
their distance to the opening 34 of the inlet capillaries
10 (snifting line 36). In an idle position, the lines 38, 40,
46 rest above the snifting line 36 until they are needed.

The above system serves for a successive analysis of N_2 and
 CO_2 . Thus, a gas sample containing N_2 and CO_2 , for example,
15 is supplied together with helium as a carrier gas in a
volumetric rate of flow of 60 ml/min via the line 16 in the
position according to Fig. 2. The small coupling tube 26
has an inner diameter of approximately 1 mm. The portions
of the lines 16, 46, 38, 40, 36 which are inside the small
20 coupling tube 26 are designed as capillaries in a
correspondingly fine manner. The volume of the gas entering
into the small coupling tube 26 via the opening 32 is such
that all secondary air is displaced from the region of the
bottom 28. Furthermore, gas which possibly emerges from the
25 openings 48, 42, 44 in the position shown in Fig 2 does not
reach the bottom area. Thus, the gas flowing into the
opening 34 of the throttling line 36 is always only a
fraction of the gas coming from the line 16. The throttling
line 36 has a precisely defined cross-section so that under
30 constant compression ratios a constant gas supply to the
mass spectrometer is ensured.

At times, a reversal of the lines takes place in order to
supply a reference gas. For example a nitrogen gas N_2 with
35 a known standardized isotope ratio can be supplied via line
40. This is done by lowering the line 40 by operating lever
53. As a result the opening 44 is located underneath the
opening 34 so that the throttling line 36 is supplied with

1 a mixture of reference gas and helium. Expediently, this
operation takes place in an interval in which no sample gas
emerges from the opening 32 or in which the line 16 is
pulled out up to a level above the opening 34. The
5 alternation between the sample gas via the line 16 and the
reference gas via the line 40 is repeated several times.

After the measurement of the nitrogen gas N_2 , the
measurement of carbon dioxide takes place. As before, the
10 sample gas flows into the small coupling tube 26 via the
line 16 similar to the above-described procedure. The
introduction of a reference gas via the line 38 is carried
out in the above-described manner by means of an
appropriate lever 52 (CO_2 with standard isotope ratio and
15 helium as carrier gas) as well. The mass spectrometer is,
accordingly, readjusted from the masses for nitrogen
isotopes to the masses of carbon isotopes.

The reading of the mass spectrometer 20 depends on the
number of ions of the supplied sample gas. In the analysis
of organic compounds or compound mixtures normally much
more CO_2 is produced for the analysis than N_2 , and supplied
with helium as carrier gas to the mass spectrometer 20 via
the open split 18. In other words, the quantity of gas
25 flowing in through the throttling line 36 at first contains
a very large proportion of helium, a fraction of N_2 and,
compared to the latter, a much larger proportion of CO_2 . In
order to attain a very high precision of measurement, the
quantity of helium should possibly be equal relative to
30 both gases. At the same time, an adjustment of the maximum
 CO_2 value to the maximum N_2 value is advantageous for the
evaluation. For this purpose, a dilution with additional
carrier gas takes place during the analysis of CO_2 . For
this purpose, a further quantity of helium is introduced
35 into the small coupling tube 26 via the line 46. To control
this quantity, the line 46 is axially moveable by means of
the lever 51. Each time the opening 48 of the capillaries
46 (line) immerses into the space underneath the opening 34

1 of the sniffling capillaries 36, the sample gas emerging
from the opening 32 is diluted with carrier gas. The gas
which is passed into the capillaries and into the mass
spectrometer via the opening 34 is thereby diluted until
5 the proportion of helium relative to the CO_2 is
approximately equal to the proportion of helium as it was
before relative to the N_2 .

10 In a further embodiment, the control of the gas supply is
attained, in addition to or instead of the variation of the
depth of immersion of the individual lines by means of the
levers 51 to 53, by a limitation of the gas flow in the
lines themselves, for example by means of appropriate
15 valves. The switching over from the sample gas in the
analysis of N_2 to a corresponding reference gas N_2 can thus
take place by throttling the line 16 and opening the line
40. Both lines should end in the area of the bottom 28.
Similarly, switching over to a reference gas CO_2 in the
analysis of CO_2 can take place by throttling the line 16
20 and opening the line 38, also with openings 32, 42 in the
region of the bottom 28. Additionally, in this case, it is
necessary to control the gas for dilution by turning on the
line 46 or deeply immersing the line 46 when it is open.

25 An example for carrying out the movement of lines inside of
a small coupling tube will be explained below by means of
Figs. 3 and 4. A small coupling tube referred to as pipette
54 (corresponding to the small coupling tube 26), is fixed
to a stand 55. Also fixedly connected thereto is a cylinder
30 56 of a piston-cylinder unit as well as a retaining plate
57. The latter carries a support 58 for the accommodation of
two capillaries 59, 60 (lines). These capillaries both
reach into the pipette 54 with corresponding openings 61,
62.

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A piston 63 which can be drawn out of the piston-cylinder
unit (cylinder 56) carries a retaining plate 64. A support
65 is fixed thereto for the accommodation of a further

1 capillary 66. The piston is vertically adjustable by
admitting compressed air to the piston-cylinder unit
(flexible tube connection 67). Accordingly, the capillary
66 is moved up or down in the pipette.

5 For the sake of clarity, only one moveable capillary 66 is
shown in Figs. 3, 4. According to the invention, more than
one capillary may be provided. For this purpose the
capillaries may immerse into the pipette 54 in curved
10 shape, corresponding to the capillaries 59, 60. For example
so-called fused silica capillaries are both flexible and
axially moveable.

In the example shown in Figs. 3 and 4, the capillary 59
15 with an inner diameter of 0.1 mm is provided for the
introduction of helium, if necessary in connection with a
sample gas. The capillary 66 has an inner diameter of 0.05
mm and is provided for the introduction of a reference gas
The capillary 66 ends in an opening 68 in an adjustable
20 region, preferably between the openings 61, 62. Finally,
the capillary 60 is provided as a sniffing line, that is to
say as a line with an inner diameter of 0.05 mm which leads
to the mass spectrometer.

25 In the present example, a pneumatic actuation is provided
for the movement of the capillaries 66. Other actuations,
for example electrical or hydraulic, are possible.

Figs. 5 and 6. relate to further embodiments of the
30 invention. Fig. 5 shows a modification compared to Fig. 2,
comprising a small coupling tube 70 which is open at both
ends. The gas supply line 16, dilution line 46, throttling
line 36 as well as the reference gas line 38 correspond to
the lines shown in Fig. 2. Just as in Fig. 2, further lines
35 may be provided in the embodiment according to Fig. 5, for
example a further reference gas line. The small coupling
tube 70 is open at an end face 72. The lines 46, 36, 38
immerse on this side (dilution line, throttling line,

1 supply line). The opposite end face 74 is partly closed or
has only a comparatively smaller inlet cross-section 76.
The gas supply line 16 coming from the element analyzer 22
enters the small coupling tube 70 via the decreased inlet
5 cross-section 76. Similar to Fig. 1, a supply from a gas
chromatograph with downstream combustion oven and
separating device may also occur.

A control of the gas concentration entering the opening 34
10 of the throttling line 36 is possible by longitudinal
displacement of the individual lines, especially 16, 38 and
46. Alternatively or additionally, the gas flows in the
individual lines can be throttled or shut off. According to
the embodiment of Fig. 5, an axial movability of the
15 reference gas supply line 38 is preferred. The movability
is indicated by a double arrow 78. In the position shown in
the figure, the reference gas moves from the dilution line
46 to the throttling line 36, if necessary, together with a
gas volume. If the reference gas supply line 38 is moved to
20 the right, practically no reference gas reaches the
throttling line 36.

Fig. 6 shows an expanded embodiment compared to Fig. 5.
Instead of one small coupling tube 70, according to Fig. 6,
25 two small coupling tubes are provided, in particular a
thicker small coupling tube 80 and a thinner small coupling
tube 82, which enters the former. The latter is open at
both ends. The small coupling tube 80 corresponds in its
structure to the small coupling tube 70, but is thicker in
30 diameter. The inner diameters of the small coupling tubes
80, 82 are approximately 3 mm and 0.7 mm, respectively.
Accordingly, the gas flow emerging from the opening 32
splits in the ratio of the end faces of the tubes
(approximately 8.5:0.5). The small coupling tube 80 thus
35 has the function of a precoupling towards the small
coupling tube 82. The reference gas and the additional
helium carrier gas enter the small coupling tube 82 via the
lines 38 and 46, are mixed in the small coupling tube 82

1 and then enter the throttling line 36. Only opening 32 is
located in the thicker small coupling tube 80.

5 A particular advantage of this embodiment is the uncoupling
of the reference gas supply from the gas supply via the
line 16 (sample supply). If different quantities of CO₂ (or
other gases) are supplied at different times, the
cross-section of the line 38 is best only for a certain
10 volumetric rate of flow. Without the described coupling of
the two small tubes 80, 82, the line 38 would have to be
replaced with another line with appropriate diameter each
time. In the embodiment according to Fig. 6, surplus
reference gas can emerge via the coupling between the two
small tubes 80, 82. Moreover, there are further advantages.
15 Under normal operation, according to the description of
Figs. 1 to 5, significantly reduced consumptions of the
reference gas and the auxiliary helium flow (line 46) can
be attained. For controlling the reference gas supply, the
volumetric flow rate is variably adjustable by means of the
20 line 46, preferably between 0 and 20 ml/min. The opening 48
is located closely in front of the end 84 of the small tube
82 which is located inside of the small tube 80. The
opening 34 is located approximately centrally in the small
tube 82. A very small volumetric flow rate from the opening
25 48 already causes a partial displacement of the sample gas
emerging from the opening 32. The latter does not enter
into the small tube 82, but, on the contrary, exits via the
end face 72. As a result a dilution of the sample gas can be
attained with significantly reduced carrier gas supply.

30 Just like in the embodiment according to Fig. 1 to 4,
axial movements of the lines would be possible in this
embodiment by levers not shown.

35 Approximately a third or one half of the thinner coupling
tube 82 is located within the thicker small tube 80. The
opening 32 is located at a distance in front of the end 84.
The dimensions of the thinner small tube 82 correspond to

1 those of the small tube 70 or 54. The small tube 80 has
approximately the same length but is substantially thicker.
A throttle valve in the tubing 46 is designated by the
reference numeral 86.

5 The small tubes 70, 80, 82 and the capillaries (lines 36,
38, 46, 16) can be fixed and moved just as shown in the
representation in Fig. 3.

10 Organic compounds may contain further elements in addition
to carbon and nitrogen, for example sulphur. In this case,
gaseous SO_2 would result from the combustion. The
corresponding isotope ratio can be determined in the
described manner, just as the isotope ratios of further
15 elements.

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Process for the analysis of gaseous components by mass spectrometry

C l a i m s :

- 1 1. Process for the analysis of several, especially two,
gaseous components by mass spectrometry, the components
being supplied, simultaneously or successively, with a
carrier gas to a mass spectrometer, the first component
5 having a different volume ratio relative to the carrier gas
compared to the second component, characterized in that, in
the analysis of a component which is provided in a greater
ratio relative to the carrier gas, the concentration of
this component is decreased by additional supply of carrier
10 gas.
2. Process according to claim 1, characterized in that
the dilution with additional carrier gas is carried out in
the region of an open split (18) known per se.

1 3. Process according to claim 1 or 2, characterized in
that the dilution with carrier gas continues until the
concentrations of the gases to be analyzed, especially CO₂
and N₂ in the carrier gas helium, become approximately
5 equal.

4. Apparatus for the provision of gaseous samples for
the analysis by mass spectrometry comprising a so-called
open split (18), at least one supply line (16) as well as
10 especially at least one reference gas supply line (38, 40)
and a throttling line (36) which leads from the open split
to the ion source of a mass spectrometer (20), where the
gas can be fed to the throttling line (36) alternately from
one of the supply lines (16, 38, 40) approximately under
15 atmospheric pressure, characterized in that a further
supply line (dilution line 46) is provided, via which a
further gas can be fed to the throttling line (36) in
addition to the gas emerging from one of the other supply
lines (16, 38, 40) for dilution of same.

20 5. Apparatus according to claim 4, characterized in
that, in the region of the open split (18), an outlet
opening (32) of the gas supply line (16) is disposed
adjacent to an inlet opening (34) of the throttling line
25 (36) in a manner known per se, and that in the region near
the inlet opening (34) the dilution line (46) with its
outlet opening (48) can be moved in and out.

6. Apparatus according to one of the claims 4 or 5,
30 characterized in that the reference gas supply lines (38,
40) can each be moved in and out in the region near the
inlet opening (34) of the throttling line (36).

7. Apparatus according to one of the claims 4 to 6,
35 characterized in that the open split (18) takes the form of
a small coupling tube (26) preferably open at one end, into
which the lines (16, 46, 38, 40) are inserted as
capillaries from at least one open end face (30).

1 8. Apparatus according to claim 7, characterized in
that the capillaries of the dilution line (46) and/or of
the reference gas lines (38, 40) are moveable in the
longitudinal direction of the small coupling tube (26) and
5 inside of same.

9. Apparatus according to one of the claims 4 to 8,
characterized by the following features:

- 10 a) the open split has two small coupling tubes (80,
82),
- b) a portion of the thinner small tube (82) is inserted
in the thicker small tube (80),
- 15 c) at least the throttling line (36), the dilution line
(46) and the reference gas supply line (38) end in
the thinner small tube (82),
- 20 d) the supply line (16), from which the sample gases to
be analyzed emerge, ends in the thicker small tube
(80),
- 25 e) the cross-sectional surface of the small tube (80)
is substantially greater than, especially 10 - 20
times the cross-section of the thinner small tube
(82), so that the surplus gas volume from the small
tube (82) can emerge from the open split via the end
face (72) of the thicker small tube (80).
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17
Patents Act 1977

Examiner's report to the Comptroller under Section 17
(The Search report)

Application number
GB 9324729.4

Relevant Technical Fields

(i) UK Cl (Ed.M) G1B (BCF, BCG); G1N (NCGK)

(ii) Int Cl (Ed.5) G01N, H01J

Search Examiner
M R WENDT

Date of completion of Search
16 MARCH 1994

Databases (see below)

(i) UK Patent Office collections of GB, EP, WO and US patent specifications.

(ii) ONLINE DATABASES: WPI, CLAIMS, ANALYTICAL ABS

Documents considered relevant
following a search in respect of
Claims :-
1-9

Categories of documents

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Category	Identity of document and relevant passages	Relevant to claim(s)
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